

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : **2003-100299**

(43)Date of publication of application : **04.04.2003**

---

(51)Int.Cl.

**H01M 4/62**

**H01M 10/40**

---

(21)Application number : **2001-289295** (71)Applicant : **TDK CORP**

(22)Date of filing : **21.09.2001** (72)Inventor : **KOSUDA ATSUKO  
MIYAKI YOUSUKE  
MARUYAMA SATORU**

---

## (54) LITHIUM SECONDARY BATTERY

(57)Abstract:

**PROBLEM TO BE SOLVED:** To suppress the decrease in the recovery capacity of a lithium secondary battery when it is reserved at a high temperature, where the decrease in the recovery capacity occurs when BF (boron-fluoride) salt is used for an electrolyte.

**SOLUTION:** The lithium secondary battery comprises a positive electrode containing PVDF (polyvinylidene fluoride) homopolymer synthesized by an emulsion polymerization method and a small amount of niobium, and negative electrode containing styrenebutadiene rubber and carboxymethylcellulose, and an electrolyte containing lithium fluoroborate and lactone.

---

## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against

examiner's decision of rejection]

[Date of extinction of right]

---

## CLAIMS

---

[Claim(s)]

[Claim 1] The PVDF homopolymer compounded by the emulsion-polymerization method at the positive-electrode side and the niobium of a minute amount, and the lithium secondary battery which has styrene butadiene rubber and a carboxymethyl cellulose in a negative-electrode side, and contains the salt and lactone of a fluoride boron acid lithium system in an electrolyte further.

[Claim 2] The rechargeable lithium-ion battery of claim 1 whose volume ratios of annular carbonate:lactone annular carbonate is further contained in the solvent of said electrolyte, and are 6:4-1:9, [Claim 3] Said positive electrode is the rechargeable lithium-ion battery of claims 1 or 2 to carry out 0.1-0.4 mass % content about niobium (Nb).

[Claim 4] One lithium secondary battery of claims 1-3 whose molecular weight of said PVDF is 80,000 or more.

[Claim 5] Said electrolyte is one rechargeable lithium-ion battery of claims 1-4 which are the solid electrolytes made to gel and contain the salt of said PVDF homopolymer, lactone, and a fluoride boron acid lithium system in this solid electrolyte.

[Claim 6] Said electrolyte is one rechargeable lithium-ion battery of claims 1-5 to carry out 1-2 mass % content in vinylene carbonate or vinyl ethylene carbonate as an additive.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the electrode presentation for cell ingredients, such as a lithium ion battery.

[0002]

[Description of the Prior Art] By remarkable development of a pocket device in recent years, the need of the cell division lithium ion battery used as a pocket device power source has been increasing quickly. Furthermore, the improvement of high-energy-izing and the cell property accompanying it serves as a target of ED with the increment in the function of a pocket device.

[0003] Meanwhile, the following item is mentioned as an important technical technical problem.

(1) An improvement of the improvement (3) cycle property of the improvement (2) elevated-temperature preservation property of safety (overcharge) [0004] LiPF<sub>6</sub> already indicated about the elevated-temperature preservation property in this if it is the salt and rechargeable lithium-ion battery which are used for a fuel cell subsystem, and LiBF<sub>4</sub>

LiClO<sub>4</sub> of the salt of other imide systems etc. -- thermal stability is considered to be a cause. A new lithium salt compound which is further indicated by the \*\* table No. 608340 [ 2000 to ] official report is also proposed in recent years, and practical use is presented.

[0005] Moreover, it is thought that the moisture in the electrochemical stability of the solvent used for the electrolytic solution and a solvent is also related as other factors, and an additive, application of various solvents, etc. are considered. Thus, improving an elevated-temperature preservation property, maintaining other cell properties, although various technique as a cure against elevated-temperature preservation is tried has a difficult point from a viewpoint which takes balance of the whole property.

[0006] As an example, it is LiBF<sub>4</sub>. The case where it is used as an electrolyte salt is explained. This LiBF<sub>4</sub> salt (it omits Following BF) has thermal stability, although conductivity is low compared with LiPF<sub>6</sub> (it omits Following PF), therefore change of an elevated-temperature preservation property, for example, the cell internal impedance by the alternating current measurement after preservation, becomes small compared with the time of using PF system.

[0007] However, LiBF<sub>4</sub> Since conductivity is low, the usual 1 C-battery capacity will decrease compared with PF system cell. For this reason, when using BF as an electrolyte salt, although the technique which an electrolytic-solution solvent presentation needs to be controlled and accompanied it has also been indicated in consideration of such a viewpoint, capacity cannot say that the point of falling compared with PF system was solved.

[0008] Furthermore, it is the technical problem from which recovery of cell \*\*\*\*\* after saving a cell also poses a problem practically. In the case of BF system especially mentioned above, recovery capacity was falling compared with EC system, and it had become the technical problem which should be improved practically.

[0009]

[Problem(s) to be Solved by the Invention] The purpose of this invention is offering the possible lithium secondary battery of preventing the fall of the cell capacity recovery after elevated-temperature preservation in the fuel cell subsystem which used BF system salt.

[0010]

[Means for Solving the Problem] That is, the above-mentioned purpose is attained by the configuration of the following this inventions.

(1) The PVDF homopolymer compounded by the emulsion-polymerization method at the positive-electrode side and the niobium of a minute amount, and the lithium secondary battery which has styrene butadiene rubber and a carboxymethyl cellulose in a negative-electrode side, and contains the salt and lactone of a fluoride boron acid lithium system in an electrolyte further.

(2) Rechargeable lithium-ion battery of the above (1) whose volume ratios of annular carbonate:lactone annular carbonate is further contained in the solvent of said electrolyte, and are 6:4-1:9 (3) Said positive electrode is the above (1) to carry out or the rechargeable lithium-ion battery of (2) 0.1-0.4 mass % content about niobium (Nb).

(4) One lithium secondary battery of above-mentioned (1) - (3) whose molecular weight of said PVDF is 80,000 or more.

(5) Said electrolyte is one rechargeable lithium-ion battery of above-mentioned (1) - (4)

which is the solid electrolyte made to gel and contains the salt of said PVDF homopolymer, lactone, and a fluoride boron acid lithium system in this solid electrolyte. (6) Said electrolyte is one rechargeable lithium-ion battery of 1 - 2 mass % above-mentioned [ to contain ] (1) - (5) in vinylene carbonate or vinyl ethylene carbonate as an additive.

[0011]

[Function] this invention persons examined various examination, especially the class of binder in the detail for the purpose of optimizing an electrode configuration to the above-mentioned technical problem, and diffusing the lithium ion in the interior of an electrode promptly. Consequently, the combination of a binder found out having influenced the cell property of BF system.

[0012] That is, the recovery capacity after elevated-temperature preservation is sharply improved compared with the former by using an SBR system rubber ingredient and CMC as a binder by the side of a PVDF system and a negative electrode as a binder by the side of a positive electrode. About this operation, although it looks when it uses BF salt that the impedance by the side of an after [ preservation ] negative electrode usually increases remarkably, by this examination result, a small thing becomes clear and the increment in an impedance is also considered that this is connected with the improvement of recovery capacity.

[0013] Moreover, the lithium cell of this invention is applicable not only to the cell which used the conventional electrolytic solution and a conventional separator but the thing using the gel system solid electrolyte which attracts attention in recent years. This cell differs also from the organic solid electrolyte with which a lithium ion conducts the inside of the giant-molecule medium by which past research has been done, and high current discharge is possible for it.

[0014]

[Embodiment of the Invention] the lithium secondary battery of this invention has styrene butadiene rubber and a carboxymethyl cellulose in the PVDF homopolymer which resembled the positive-electrode side and was compounded by the emulsion-polymerization method and the niobium (Nb) of a minute amount, and a negative-electrode side, and contains the salt and lactone of a fluoride boron acid lithium (BF) system in the electrolytic solution further.

[0015] That is, as for a positive-electrode side, a negative-electrode side uses a carboxymethyl cellulose (CMC) for rubber system latex ingredients, such as styrene butadiene rubber (SBR), and a pan as an addition component, using PVDF (polyvinylidene fluoride) as a binder of an electrode. Furthermore, lactone, such as gamma-butyrolactone, is used as a constituent as a gelation solid electrolyte component. Moreover, annular carbonate, especially ethylene carbonate (EC) are preferably used as an electrolyte solvent.

[0016] Consequently, even when BF system salt is used as an electrolyte salt, in spite of using the salt of BF system by making the electrolytic solution contain lactone using PVDF compounded by the emulsion-polymerization method as a binder, and SBR and CMC, the recovery capacity fall after elevated-temperature preservation can be sharply reduced compared with the former.

[0017] Only when gamma-butyrolactone is made [ and ] to exist in the electrolytic solution by using styrene butadiene rubber (SBR) as a negative-electrode side binder,

using a carboxymethyl cellulose (CMC) as an addition component, using this polyvinylidene fluoride homopolymer (henceforth, PVDF) as a positive-electrode side binder, the fall phenomenon of the capacity in a fluoride boron acid lithium system (following BF system) can be made to control according to this invention.

[0018] When PVDF by other synthetic approaches is used, and when it is not the combination of SBR and CMC, such effectiveness is not seen at all. Therefore, when making an electrode form into a high energy consistency, it is a very effective means.

[0019] Although it is not certain at present about the mechanism, there is the active spot which is inherent in PVDF, the bloating tendency resulting from that resistance decreases by the interaction of a salt with BF system inside an electrode and the crystalline difference in resin improves, and diffusion of a lithium becomes easy and is \*\*\*\*(ed) with what also reduces the fall of cell capacity by half compared with the former as a result. Moreover, the ester group of the CMC origin etc. exists in a negative-electrode front face by using SBR and CMC together, and it acts, in case a negative-electrode coat is formed at the time of charge, and if they are usual, while they will prevent decomposition of the lactone which is easy to be consumed at the time of coat formation, they are presumed that formation of a more precise coat is made.

[0020] It is indicated by JP, 8-250127, A etc. about the point using an emulsion-polymerization method. an emulsion-polymerization method -- for example, -- substantial -- the bottom of anoxia -- the inside of a water medium -- an iodine compound or a bromine compound -- desirable -- Jo -- base -- the method of performing the bottom emulsion polymerization of existence of a radical initiator is listed to the bottom of existence of a compound, agitating a par halo olefin and under pressurization of the monomer which will give at least a hard spot if it requires.

[0021] Extremely, it is got blocked and, as for one advantage using the homopolymer obtained by the emulsion-polymerization method, the polymer whose polymer of a high grade, i.e., an impurity, is the amount of traces and whose impurity is the amount of the ppb (part per million) range is obtained.

[0022] Especially the degree of crystallinity of the homopolymer obtained by this emulsion-polymerization method is about 35 - 55% 30% or more. Moreover, as the molecular weight, 80,000 or more are desirable, and especially 100,000-140,000 are desirable.

[0023] A constituent with an electric conduction assistant is preferably used for an electrode according to an electrode active material, a binder, and the need.

[0024] A carbon material is used for a negative electrode as an active material. An electric conduction assistant is added to a negative electrode if needed, and a carboxymethyl cellulose (CMC) is further used as an additive, using styrene butadiene rubber (SBR) as a binder.

[0025] The styrene butadiene rubber (SBR) used as a binder has a good adhesive property to a negative-electrode charge collector, and maintains the adhesive strength stabilized also under the elevated temperature. The carboxymethyl cellulose (CMC) contained as an additive is used in order to perform thickening processing to a carbon material. After this processing is performed, good coating liquid can be obtained by mixing with SBR.

[0026] It is desirable to use positive active material for a positive electrode for the oxide which a lithium ion can intercalation deintercalate. Furthermore, in addition to said active material, in a positive electrode, the niobium (Nb) of a minute amount is contained

preferably. Moreover, as a binder, the PVDF homopolymer compounded by the describing [ above ] emulsion-polymerization method is used.

[0027] The lithium secondary battery of a good property can be obtained by using such an electrode.

[0028] What is necessary is just to choose suitably from for example, a meso carbon micro bead (MCMB), a natural or artificial graphite, a resin baking carbon material, carbon black, a carbon fiber, etc. the carbon material used as an electrode active material. These are used as powder except for a carbon fiber. A carbon fiber is desirable also in these, moreover, a graphite -- desirable -- the mean particle diameter -- 1-30 micrometers especially -- 5-25 micrometers it is -- things are desirable. When mean particle diameter is too small, it is in the inclination for a charge-and-discharge cycle life to become short, and for dispersion in capacity (individual difference) to become large. If mean particle diameter is too large, dispersion in capacity will become remarkably large and average capacity will become small. It is thought of for dispersion to arise in contact to a graphite and a charge collector, or contact of graphites that dispersion in capacity arises when mean particle diameter is large.

[0029] As oxide which a lithium ion can intercalation deintercalate, the multiple oxide containing a lithium is desirable, for example,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ ,  $\text{LiV}_2\text{O}_4$ , etc. are mentioned. The mean particle diameter of the powder of these oxides is 1-40 micrometers. It is desirable that it is extent.

[0030] In addition to said active material, the niobium (Nb) element of a minute amount is contained in a positive electrode. The contents of the niobium (Nb) in a positive electrode are 0.1 - 0.4 mass %, especially 0.12 - 0.35 mass % preferably. If there are too many contents of niobium, the fall of capacity will be caused, and if too few, the capacity recovery after elevated-temperature preservation and a subsequent cycle property will get worse.

[0031] An electric conduction assistant is added as occasion demands by the electrode. As an electric conduction assistant, metals, such as a graphite, carbon black, a carbon fiber, nickel, aluminum, copper, and silver, are mentioned preferably, and especially a graphite and carbon black are desirable.

[0032] In a negative electrode, the range of active material:electric conduction assistant:SBR:CMC=85-95:2-8:2-5:1-2 is desirable at a weight ratio, and an electrode presentation is an active material:electric conduction assistant at a weight ratio with a positive electrode :P The range of VDF homopolymer=85-92:5-9:3-6 is desirable.

[0033] First, manufacture of an electrode distributes an electric conduction assistant in a binder solution an active material, a binder, and if needed, and prepares coating liquid.

[0034] And this electrode coating liquid is applied to a charge collector. What is necessary is not to limit especially a means to apply but just to determine it suitably according to the quality of the material, a configuration, etc. of a charge collector. Generally, metal mask print processes, electrostatic spray painting, a dip coating method, a spray coating method, the roll coat method, a doctor blade method, the gravure coat method, screen printing, etc. are used. Then, a monotonous press, a calendaring roll, etc. perform rolling processing if needed.

[0035] What is necessary is just to choose a charge collector from the usual charge collector suitably according to the configuration of the device which a cell uses, the configuration method of the charge collector into a case, etc. Generally, aluminum etc. is

used for a positive electrode and copper, nickel, etc. are used for a negative electrode. In addition, as for a charge collector, a metallic foil, a metal mesh, etc. are usually used. Although contact resistance with an electrode becomes small rather than a metallic foil in the metal mesh, contact resistance also with a sufficiently small metallic foil is obtained.

[0036] And a solvent is evaporated and an electrode is produced. Coating thickness is 50-300 micrometers. Considering as extent is desirable.

[0037] Although especially the structure of a <lithium secondary battery> lithium secondary battery is not limited, it consists of a positive electrode, a negative electrode, and a separator, and is usually applied to a laminating mold cell, a cylindrical cell, etc.

[0038] The laminating of such a positive electrode, a separator, and the negative electrode is carried out to this order, they are stuck to it by pressure, and it considers as a cell element assembly.

[0039] Generally the electrolytic solution into which a separator is infiltrated consists of an electrolyte salt and a solvent. as an electrolyte salt -- LiBF<sub>4</sub>, LiPF<sub>6</sub>, LiAsF<sub>6</sub>, LiSO<sub>3</sub>CF<sub>3</sub>, LiClO<sub>4</sub>, and LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> etc. -- although lithium salt can be mentioned -- this invention -- LiBF<sub>4</sub> etc. -- a fluoride boron acid system lithium is used.

[0040] As a solvent of the electrolytic solution, lactone, such as gamma-butyrolactone, should just surely exist. When considering as the mixed solvent of lactone and other solvents, if compatibility with a separator and an electrolyte salt is good, although especially a limit is not carried out, the polar organic solvent to which decomposition does not take place with high operating voltage with a lithium cell, either is desirable [ other solvents ]. For example, the ring type ether, such as the ring type ether, such as carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, dimethyl carbonate (DMC), diethyl carbonate, and ethyl methyl carbonate, a tetrahydrofuran (abbreviated name THF), and 2-methyl tetrahydrofuran, 1, 3-dioxolane, and 4-methyl dioxolane, a sulfolane, etc. can be mentioned.

[0041] In this invention, lactone, such as gamma-butyrolactone, is contained at least in the solvent of the electrolytic solution. Moreover, in combination with lactone, such as this gamma-butyrolactone, annular carbonate, such as EC, is desirable in the above-mentioned solvent. Moreover, the volume ratio of annular carbonate and lactone converts into ethylene carbonate and gamma-butyrolactone, and depends 6/4 - 1/9 preferably, and it is preferably desirable 3 / 7 - 1/9, and that it is especially 1 / 3 - 3/17.

[0042] The concentration of the electrolyte salt at the time of thinking that the electrolytic solution is constituted from a solvent and an electrolyte salt is 0.3 - 5 mol/l preferably. Usually, the highest ion conductivity in the 0.8 - 2.0 mol/l neighborhood is shown.

[0043] As for the solid electrolyte thru/or separator sheet which forms a separator, it is desirable to use what was manufactured by the above-mentioned polyvinylidene fluoride homopolymer, especially the emulsion-polymerization method.

[0044] As for the fine porosity film for solid electrolytes used by this invention, it is desirable to form by the wet phase separation method shown below.

[0045] A wet phase separation method is an approach of performing phase separation in a solution, in membrane formation by the solution casting method. That is, it is made to dissolve in the solvent in which this polymer may dissolve the polymer used as the fine porosity film, the obtained membrane formation undiluted solution is applied to homogeneity on base materials, such as a metal or plastic film, and the film is formed. Then, it is the approach of obtaining the fine porosity film by introducing the membrane

formation undiluted solution which carried out the cast to the shape of film into the solution called a coagulation bath, and producing phase separation. Spreading of a membrane formation undiluted solution may be performed in a coagulation bath.

[0046] The adhesives for raising the adhesive property of the above-mentioned fine porosity film and an electrode may be used. Polyolefine system adhesives, such as a uni-urinal stall (Mitsui Chemicals, Inc. make), SBR (Nippon Zeon Co., Ltd. make), AKUA tex (CHUORICA CO., LTD. make), and ADOKOTO (made in Morton), etc. can be mentioned, and, specifically, AKUA tex etc. is desirable especially.

[0047] Organic solvents, such as water or toluene, are dissolved or distributed, and adhesives are adhered and arranged by spraying, spreading, etc. at the fine porosity film. [0048] The void content of the fine porosity film is 70 - 80% more preferably 50 to 90% 50% or more. Moreover, an aperture is 0.02 micrometers. It is 2 micrometers above. It is 0.02 micrometers preferably hereafter. It is 1 micrometer above. It is 0.04 micrometers more preferably hereafter. It is 0.8 micrometers above. It is 0.1 micrometers especially preferably hereafter. It is 0.8 micrometers above. It is 0.1 micrometers still more preferably hereafter. It is 0.6 micrometers above. It is the following, the thickness of the fine porosity film -- desirable -- 20-80 micrometers more -- desirable -- 25-45 micrometers it is .

[0049] The melting point is desirable and, as for the fine porosity film, it is desirable that 160-170 degrees C and the heat of fusion are especially formed with the ingredient of 40 - 60 J/g especially preferably 30 or more J/g 150 degrees C or more.

[0050] Other gel mold macromolecules may be used for a separator. For example, polyalkylene oxide, such as (1) polyethylene oxide and polypropylene oxide, (2) The copolymer of ethyleneoxide, the copolymer of acrylate and (3) ethyleneoxides, and the glycol ether, (4) The copolymer of ethyleneoxide, the glycol ether, and the allyl compound glycol ether, (5) Polyacrylate (6) polyacrylonitrile (7) polyvinylidene fluoride, A vinylidene fluoride-hexafluoropropylene copolymer, a vinylidene fluoride-chlorination 3 fluoride ethylene copolymer, Fluorine system macromolecules, such as a vinylidene fluoride-hexafluoro pro bilene fluororubber and a vinylidene fluoride" tetrafluoroethylene-hexafluoropropylene fluororubber, etc. are mentioned.

[0051] A gel macromolecule may be mixed with the electrolytic solution, and may apply to a separator. Furthermore, a gel macromolecule may be made to construct a bridge with ultraviolet rays, EB, heat, etc. by putting in an initiator.

[0052] the thickness of a solid-state-like electrolyte -- 5-100 micrometers Further 5-60 micrometers especially -- 10-40 micrometers it is -- things are desirable. Since the solid-state-like electrolyte of this invention has strong reinforcement, thickness can be made thin. The solid-state-like electrolyte of this invention is 60 micrometers practically. Compared with the conventional gel electrolyte which was not made, thin-film-izing is below possible, and it can do further more thinly than the separator (usually 25 micrometers) currently used in the lithium ion battery of a solution system. Therefore, the formation of a thin large area which is one of the advantages using a solid-state-like electrolyte, i.e., the formation of a sheet-like gestalt, is possible.

[0053] As other separator components, there are a kind of polyolefines, such as polyethylene and polypropylene, or two sorts or more (in the case of two or more sorts, there is a lamination object of the film more than a bilayer etc.), polyester like a polyethylene tele FUTA rate, thermoplastic fluororesins like an ethylene-



tetrafluoroethylene copolymer, and celluloses. For the permeability measured by the approach of specifying to JIS-P8117, 5 - 2000 seconds / about 100 cc, and thickness are [ the gestalt of a sheet ] 5-100 micrometers. There are a fine porosity film which is extent, textile fabrics, a nonwoven fabric, etc.

[0054] 1-2 mass % extent content of vinylene carbonate and the vinyl ethylene carbonate is preferably carried out as an additive at an electrolyte. by containing such an additive, an early cycle property improves, and thereby, a cycle property is also boiled markedly and is improved over a long period of time. Moreover, an impedance is reduced and an electrical property also becomes good.

[0055] The sheathing bag is constituted from a laminate film with which the laminating of polyolefin resin layers and heat-resistant polyester resin layers, such as polypropylene as a heat adhesive property resin layer and polyethylene, was carried out by both sides of metal layers, such as aluminum. A sheathing bag carries out heat adhesion of both the heat adhesive property resin layers of those end faces of three sides for the laminate film of two sheets beforehand, forms the 1st seal section, and is formed in saccate [ in which one side carried out opening ]. Or the laminate film of one sheet is turned up, heat adhesion of the end face of both sides is carried out, the seal section is formed, and it is good also as saccate.

[0056] In order to secure the insulation between the metallic foil which constitutes a laminate film, and a derivation terminal as a laminate film, it is desirable to use the laminate film which has the laminated structure of a heat adhesive property resin layer / polyester resin layer / metallic foil / polyester resin layer from an interior side. Since it remains by using such a laminate film at the time of heat adhesion, without a high-melting polyester resin layer melting, the clearance of a derivation terminal and the metallic foil of a sheathing bag can be secured, and an insulation can be secured. Therefore, the thickness of the polyester resin layer of a laminate film is 5-100 micrometers. Considering as extent is desirable.

[0057]

[Example] Hereafter, this invention is explained using an example.

[0058] As a <example 1> electrolyte membrane, the fine porosity film was produced using the following ingredient, and it considered as the solid-state-like electrolyte using this.

[0059] The polyvinylidene fluoride [Elf Atochem (ATOFUINA) make and Kynar 741] 20 weight section is dissolved in the mixed solution which consists of the dimethylacetamide 40 weight section and the dioxane 40 weight section, a doctor blade method is used, and it is 200 micrometers. It cast into thickness on the glass plate.

[0060] the stream after being immersed in the coagulation bath which consists of the dioxane 80 weight section and the water 20 weight section immediately for 10 minutes and making it solidify after flow casting -- 60 degrees C after washing for 30 minutes in inside -- 1 hour -- drying -- 50 micrometers in thickness The fine porosity film which consists of a polyvinylidene fluoride homopolymer was obtained.

[0061] the void content of the obtained fine porosity film -- 70% and aperture:0.2micrometer it was .

[0062] In order to give an adhesive property to the above-mentioned fine porosity film front face, a polyolefine system ingredient may be made to deposit with a spray etc.

[0063] And it is electrolytic-solution (it abbreviates to EL) 2M to this solid-state-like

electrolyte sheet. Vinylene carbonate 1 mass % was added to LiBF<sub>4</sub>/EC+ gamma-butyrolactone (EC/gamma-butyrolactone = 2/8 (volume ratio)), it carried out thing sinking in, and the solid-state-like electrolyte was obtained.

[0064] Furthermore, the cell was produced using the obtained solid-state-like electrolyte.

[0065] It is LiCoO<sub>2</sub> as positive active material. The polyvinylidene fluoride homopolymer which compounded acetylene black by the describing [ above ] emulsion-polymerization method as a binder was used as an electric conduction assistant.

[0066] It is LiCoO<sub>2</sub> at a weight ratio. : Acetylene black : P Weighing capacity was carried out so that it might be set to VDF=87:8:5, and in addition, these were mixed under the room temperature and it considered as the slurry for positive electrodes so that n-methyl pyrrolidone (NMP) might be further set to NMP:PVDF=9:1 (weight ratio).

[0067] moreover -- as a negative-electrode active material -- a meso carbon micro bead (MCMB) -- as an electric conduction assistant, SBR was used as a binder and CMC was used for acetylene black as a dispersant.

[0068] a weight ratio -- MCMB:acetylene black: -- weighing capacity was carried out so that it might be set to SBR:CMC=90:5.5:3:1.5, and in addition, MCMB and acetylene black were added to this and it considered as the paste so that pure water might be further set to pure-water:CMC=98:2 (weight ratio). Subsequently, the dispersion liquid which adjusted pure water so that it might be set to pure-water:SBR=1:1 (weight ratio) were added to the above-mentioned paste, were prepared, and it considered as the slurry for negative electrodes.

[0069] And the slurry for positive electrodes and the slurry for negative electrodes which were obtained were applied on aluminium foil and copper foil with the doctor blade method, respectively, at 100 degrees C - 130 degrees C, evaporation desiccation was carried out and NMP or pure water was sheet-ized. The positive electrode and negative electrode which were sheet-ized were processed even into predetermined thickness by the roll press, respectively.

[0070] Thus, the solid-state-like electrolyte, positive electrode, and negative electrode which were obtained were cut in predetermined size, the laminating of each sheet was carried out, and the heat lamination was carried out at 130-160 degrees C. Then, the heat lamination of the copper grid which applied electroconductive glue to the negative electrode for the aluminum grid which applied electroconductive glue to the positive electrode beforehand as a charge collector beforehand as a charge collector was carried out. And it is 2M as the electrolytic solution to this. After infiltrating what added vinylene carbonate 1 mass % to LiBF<sub>4</sub> / EC+ gamma-butyrolactone (EC/gamma-butyrolactone = 2/8 (volume ratio)), it enclosed with the aluminum lamination pack and the lithium secondary battery was produced.

[0071] The capacity after charge of the produced sample was measured. It was based on the capacity when producing the cell of PF system about cell capacity.

[0072] In the <example 2> example 1, the electron was similarly produced and measured except having changed the electrolytic-solution presentation below.

Electrolytic-solution presentation EC / gamma-butyrolactone = 3/7 (volume ratio)

[0073] <Example 1 of a comparison> The cell of PF system was produced like the example 1 except having used the following electrolytic-solution presentation.

Electrolytic-solution presentation EC/DEC=3 / 7 (volume ratio)

Salt: 1M LiPF<sub>6</sub> [0074] PVDF from which the <example 2 of comparison> forward

negative electrode was obtained by the suspension-polymerization method as a binder Except having used KF1000 and a homopolymer, the cell was produced like the example 1 and capacity was measured.

[0075] The cell was produced like the example 1 of a comparison except having considered the <example 3 of comparison> electrolytic solution as the following electrolytic-solution presentation.

Electrolytic-solution presentation EC/DEC=4 / 6 (volume ratio)

[0076] About the above cell, the result of initial capacity and the recovery capacity after 60-degree-C preservation was summarized in Table 1.

[0077]

[Table 1]

	
---	--

[0078] In the case of examples 1 and 2, compared with the examples 1 and 2 of a comparison, it turns out that an early capacity is more than an EQC and that recovery capacity is improved to about 100% of level so that clearly from Table 1.

[0079] this -- as a gelation solid electrolyte component -- gamma-butyrolactone and a PVDF polymer -- using -- in addition -- and it is in the point of having used the PVDF polymer for the positive-electrode side shown in the example 1 as an electrode binder, and having used SBR and CMC for the negative-electrode side. This is effectiveness which a gelation solid electrolyte component and a binder begin to live together, and discover.

[0080] Moreover, in this example, although the gel system solid electrolyte was used, if Above PVDF and SBR and gamma-butyrolactone live together, the same effectiveness will be acquired also in the conventional solution system cell. Moreover, when it replaced with vinylene carbonate in the example 1 and vinyl ethylene carbonate was used, it was checked that the almost same effectiveness is acquired.

[0081]

[Effect of the Invention] According to this invention, the recovery capacity fall at the time of the elevated-temperature preservation produced in case BF system salt is used can be controlled as mentioned above.

---

[Translation done.]

---